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TECHNICAL NOTE

No. 1845

ATTEMPTS TO DEFOAM EXISTING OILS BY PROCESSING

By J. W. McBain, J. V. Robinson, W. W. Woods, and I. M. Abrams

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SUMMARY

Lubricating oil was processed by treatment with various absorbents and by solvent extraction in an attempt to reduce its intrinsic foaming ability.

Aeroshell 120 was treated by recycling it through a column of activated charcoal at temperatures of 50° C or lower, after which at 100° C it formed about one-tenth of the volume of foam as compared with the untreated oil. The charcoal deteriorated in its effectiveness after continued use. A powerful foam inhibitor was eluted from the exhausted charcoal with benzene or pyridine. The mechanism of the action of the charcoal has been considered.

The absorbents, activated magnesium oxide, silica gel, and Porocel, when packed in columns through which Aeroshell was recycled, defoamed the oil somewhat but not to such an extent as did charcoal.

Extraction of lubricating oils with the solvents - liquid sulfur dioxide, phenol, and aqueous sodium hydroxide - failed to produce any significant change in the foaming.

The greater foaming of oil upon its first test after a period of quiescence of a few hours was proved to be due to air dissolved in the oil.

Finely divided sodium chloride, dispersed into the oil and then removed by filtration, had no effect on the foam stability.

INTRODUCTION

The attack upon the practical aspects of the problem of inhibition of foaming in lubricating oils, using chemical methods, has two possible approaches; namely, to add something to the oil to prevent foaming or to remove from the oil something that causes foaming. The approach by the additive method received first attention, in view of its demonstrated success and the comparatively straightforward experimental methods involved. In reference 1, five methods were investigated by which

foaming constituents might be removed from lubricating oils. One of these methods has been developed intensively, as reported herein, namely, the removal of foaming constituents by absorption on an active surface and, in particular, upon activated charcoal. Another of these previously suggested methods, solvent extraction, has been further tried but without success. The other methods are of continued theoretical interest but are being held in abeyance until their exploitation is expedient and necessary.

In the first year of research upon the problem of foaming of lubricating oils in this laboratory, an experiment showed that treatment with activated charcoal altered the refractive index of the oil. Another experiment several months later showed that charcoal treatment significantly reduced the foaming of the oil.

In the same period, samples taken at different stages in the refining process were received from the Union Oil Company. From study of these samples, it was learned that the foaming of the crude intermediates was greatly reduced by further refining, mostly by the solvent (phenol) extraction and appreciably further by a clay treatment. Attempts still further to reduce the foaming by continued solvent extractions and clay treatment failed. In fact, subsequent experience showed that it was mere chance that the first treatment with activated charcoal was highly successful.

Although difficulty with the charcoal method followed, during which consistent results could not be obtained, progress is encouraging. Oil can be consistently defoamed by processing, and the first confusion is to a considerable extent rationalized.

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NOTATION

The following grades are used to indicate approximate foam stability:

- A no foam by bubbling methods, collapse in a few seconds by other methods
- B foaming reduced to approximately one-fifth of original
- C foaming reduced to approximately one-third to one-half of original
- D foaming reduced to less than one-half of original
- E foaming same as original
- F foaming greater than original

PROCEDURE

Treatment by Mixing Charcoal with Oil

Three general types of procedure were employed in the long series of preliminary experiments upon the defoaming of lubricating oils by treatment with activated charcoal. These differed principally in the temperature of the oil while in contact with the charcoal. The treatments made were:

- (1) At room temperature
- (2) At elevated temperature (200° to 350° C)
- (3) At temperature of an ice-water bath

The general procedures are subsequently described, and variations that appear significant for the respective samples are indicated in the tables.

Procedure at room temperature.- One to fifteen grams of charcoal was weighed into an eight-ounce bottle, and one hundred grams of oil was added. After 2 hours of mechanical stirring, the mixture was heated to 70° to 80° C and was filtered through paper on a preheated Büchner funnel. The filtrate was filtered again, if necessary, to remove traces of charcoal. The charcoal was extracted first with benzene and then with pyridine, and the solvents were evaporated on a steam bath to recover the benzene and pyridine elutriates. Other details of the experiments are summarized in table I.

Procedure at elevated temperature.- The oil and charcoal mixtures were heated, usually over an open flame, in vessels ranging from test tubes and flasks to an iron bomb. The recorded temperature of treatment was that registered by a thermometer inserted into the heated mixture. The mixture was filtered hot, the charcoal was extracted with benzene and pyridine, and the elutriates were recovered, as before described. Many variations in this procedure were employed, the most significant details of which are summarized in table II.

Procedure at low temperature.- The procedure for the low-temperature treatments with charcoal was the same as that described for room temperature, except that the bottle was immersed in an ice-water bath during the 2-hour stirring period, and low-boiling petroleum ether was added to keep the viscosity low. More petroleum ether was added to facilitate filtration, which was carried out at low temperature. A benzene elutriate was obtained from the charcoal in the previously described manner. These experiments are summarized in table III.

Treatment of Aeroshell with successive portions of charcoal.- Four liters of Aeroshell 120 was placed in a six-liter heat-resistant glass flask supported in a three-gallon boiling-water bath, and 80 grams of Granular Hydro-Darco charcoal was added. A motor-driven stirrer blade was introduced into one mixture, which was stirred at 100° C for $4\frac{3}{4}$ hours. Attempts to filter this large volume of oil through filter paper in a Büchner funnel failed, so it was poured through a fine brass screen, which removed approximately 80 percent of the charcoal but left the fines in the oil.

The charcoal was eluted with one 200-milliliter portion of petroleum ether, one 200-milliliter portion of benzene, and five 100-milliliter portions of pyridine, in that order. The elutions were made by stirring the charcoal and each portion of extracting solvent together in a beaker for 10 minutes. The portions from each of the respective solvents were combined, after filtration, and the solvents were evaporated on a water bath to yield the three elutriates.

A small portion of the oil containing charcoal fines was filtered through paper to be tested for foaming. To the rest was added a fresh batch of 80 grams of Granular Hydro-Darco charcoal. The mixture was again stirred in the flask in the water bath at 100° C and filtered through the fine brass screen. Washing of the charcoal again produced three elutriates, corresponding to the petroleum ether, benzene, and pyridine eluates. The process was repeated in the same way once again on the oil containing charcoal fines. The same portion of oil was treated in this manner with three fresh batches of Granular Hydro-Darco charcoal, as follows:

Treatment 1, $4\frac{3}{4}$ hours

Treatment 2, $1\frac{1}{2}$ hours

Treatment 3, $1\frac{3}{4}$ hours

The refractive indices of the nine elutriates were determined, using the Abbé refractometer. The elutriates were added to Aeroshell 120, in a volume proportion of 1:4, and their effect upon the foaming was evaluated by the air-bubbling method at 100° C.

Treatment by Passing Oil through Charcoal Adsorption Column

The column was supported in a 20-millimeter-diameter glass tube, about 19 inches long, constricted to a 10-millimeter tube at the bottom. A "T" into which a thermometer could be horizontally inserted, with a rubber seal, was fused below the 10-millimeter tube. A 1-liter

separatory funnel above the column served as a reservoir. Its stem passed through a rubber stopper in the top of the column. A gear pump circulated oil from the bottom of the column to the top of the reservoir through 1/4-inch pipe connected to the glass with short pieces of rubber tubing. A circulation rate of 8 to 9 liters of oil per hour was maintained by the pump, more or less independently of the oil temperature, provided the adsorbent was coarsely granular and did not pack tightly.

Twenty grams of the charcoal, Granular Hydro-Darco, was poured into the column, on top of a few inches of coarse gravel supported on a wire screen. No further tamping or packing was resorted to, since it was desired to keep the bed open and to avoid breaking the granules.

One liter of oil was poured into the open top of the reservoir, and the stopcock in the stem was opened. The oil was drawn through the column with aspirator suction. When the column was full, the pump was started and the oil was pumped back to the top of the reservoir.

Temperature was adjusted by varying the current through resistance wire wound in a loose spiral around the entire length of the column.

Test samples were drawn at timed intervals by inserting a small bottle under the pump outlet at the top of the reservoir.

At the completion of the run, the remaining oil was drained out of the column and the charcoal was rinsed with benzene, using four 250-milliliter portions. The charcoal was then dried of benzene by drawing air through the column. The benzene elutriates, when they were saved, were obtained by evaporating the benzene on a water bath. When the charcoal was no longer effective, it was withdrawn from the column, after the benzene washing, and placed in a beaker in which it was washed with pyridine to obtain a pyridine elutriate.

Treatment by Mixing Miscellaneous Sorbents with Oil

The procedure was the same as the room-temperature procedure with activated charcoal mixed with oil. In each case, 15 grams of sorbent was used for 100 grams of oil. The experimental results are summarized in table IV.

Treatment by Passing Oil through Miscellaneous Sorbents in Columns

The same column as that used for charcoal was packed with certain other adsorbents each of which was tested by the same procedure as that used for charcoal. Twenty grams of the adsorbent was used to pack the column, and one liter of oil was circulated. The circulation rate was 8 to 9 liters per hour, except in the case of Porocel which tended to pack, thus reducing the flow somewhat.

Solvent Extraction of Lubricating Oils

Phenol.-- NACA Reference Oil, Aeroshell 120, and Standard Aviation 120 were each extracted with phenol. One hundred fifty grams of oil and one hundred fifty grams of phenol were weighed in separate containers, heated to 90° C, and mixed. The mixture was shaken for several minutes in a 500-milliliter separatory funnel, the layers were allowed to separate, and the heavier phenol layer was drawn off. The extraction process was repeated again on each sample. The remaining oil and its dissolved phenol were poured into a 500-milliliter distilling flask, and the phenol was distilled at 95° to 100° C at a pressure of 5 millimeters of mercury.

Liquid sulphur dioxide.-- Aeroshell 120 (12.2 grams) and an equal weight of liquid sulfur dioxide were drawn into an evacuated glass reactor vessel, and the mixture was agitated 25 minutes at 25° C. Upon standing, the phases separated cleanly and were drawn off separately. The sulfur dioxide layer yielded 0.1 gram of a bright yellow oil upon evaporation. The oil layer was aerated to remove all the sulfur dioxide. A foam test on this oil (by aeration and evacuation) showed no difference from one on the original Aeroshell. The sample was repeatedly washed with 6 N sodium hydroxide and then with water and was dried by aeration.

Aqueous sodium hydroxide.-- Twenty milliliters of Aeroshell 120 was shaken at 40° to 50° C with two 100-milliliter portions of 20-percent sodium hydroxide solution. The phases were separated in a separatory funnel after each treatment. The oil was washed free of alkali by repeatedly shaking it with fresh portions of water. The extracted oil was tested for foaming by the method of aeration and evacuation at room temperature.

RESULTS

Treatment by Mixing Charcoal with Oil

Preliminary experiments.-- The data from all the preliminary experiments are given in tables I, II, and III for the room-temperature, elevated-temperature, and low-temperature treatments, respectively. The tables show that comparatively few of the charcoal treatments were successful.

However, the successful ones yielded spectacularly improved oils, the foaming grade A in this case representing oils which would foam only very slightly, either by bubbling at 100° C or by aeration and evacuation at room temperature.

At the completion of the work summarized in tables I, II, and III, few indications were available concerning the factors controlling the successful defoaming treatment. The data are of possible reference value when sufficient information is at hand to interpret these experiments properly.

Treatment of Aeroshell with successive portions of charcoal.- The purpose of the treatment of Aeroshell with successive portions of charcoal, which was undertaken after most of the data reported herein were on hand, was to obtain a considerable quantity of the foam-inhibiting substance, which is closely associated with the charcoal. The repetitive treatments upon the same oil were to determine whether an oil could continue to furnish this foam-inhibiting material indefinitely. The data furnish no clear-cut answer to this question because: (1) The conditions were not optimum, which is not surprising in view of previous experience and (2) the third treatment was slightly but definitely less effective than the first, although the first treatment was over twice as long.

The foaming of the filtrates, that is, the bulk of the oil, was not significantly changed by the charcoal treatment. The nine elutriates were tested for foaming by air bubbling at 100° C, when mixed with Aeroshell to comprise about one-fifth of the oil volume. Some of them showed definite defoaming action.

Treatment	Time of treatment (hr)	Effect of elutriates on foaming of Aeroshell		
		Petroleum ether	Benzene	Pyridine
1	$4\frac{3}{4}$	None	Very slight defoamer	Moderate defoamer
2	$1\frac{1}{2}$	None	None	None
3	$1\frac{3}{4}$	Very slight defoamer	Moderate defoamer	Moderate defoamer

The refractive indices of the elutriates were utilized to demonstrate that a change in composition had been brought about by the charcoal treatment. The values are summarized:

Treatment	Refractive indices from 19° to 20° C			
	Elutriate			Filtrate
	Petroleum ether	Benzene	Pyridine	
1	1.4898	1.4940	1.5000	1.4920
2	1.4886	1.4932	1.4900	
3	1.4880	1.4920	1.5001	
Aeroshell 120	1.4923			

These values show a definite pattern. All the petroleum-ether elutriates have lower refractive indices, the benzene elutriates have nearly the same or somewhat higher indices, and the pyridine elutriates have higher refractive indices than the refractive index of Aeroshell 120. The filtrate has a slightly different index, barely outside the experimental variation of the refractometer.

The yields of each of the elutriates were as follows:

Treatment	Yield of elutriates (cc)		
	Petroleum ether	Benzene	Pyridine
1	90	30	8
2	40	20	10
3	41	19	8

The best of the elutriates, the pyridine elutriates from treatments 1 and 3, were tested over a range of concentrations in Aeroshell 120, using the air-bubbling method at 100° C. The best foam inhibitor from this series was the pyridine elutriate from treatment 1, at a concentration in Aeroshell of 1.2 percent, giving a foam-volume increase of 180 percent (compared with that of 490 percent for Aeroshell). The range of concentration tested was 0.16 to 4.0 percent. The pyridine elutriate from treatment 1 was somewhat less effective in the concentration range of 0.05 to 5.0 percent. None of the fractions produced in this experiment was

at all comparable with the best obtained from the charcoal-column treatments, with regard to their foam-inhibiting action.

Treatment by Passing Oil through Charcoal Adsorption Column

The data from the satisfactory runs of the series of 12 runs made with the column packed with charcoal (Granular Hydro-Darco) are presented graphically in figure 1 in terms of the percentage volume increase of the oil samples produced by a prescribed period of bubbling in a foam meter at 100° C. Runs 4 to 11 are so charted. One batch of charcoal was used in runs 4 and 5 and another, in runs 6 to 11.

During any one run, a minimum was reached in the foaming of the oil after a certain length of treatment, and further treatment caused the oil to foam more. When the oil was removed, the charcoal washed with benzene, and fresh oil put in, the cycle would repeat itself. It was suspected from the first runs (not included) and confirmed by runs 6 to 11 that the charcoal could not thus be used indefinitely. Likewise, it was early apparent that low temperature was more beneficial to the treatment than high temperature.

There are two variables in the series of runs 6 to 11 (fig. 1(b)); namely, the decreasing effectiveness of the charcoal with use and the temperature of treatment, whose effects may be at least partly resolved. The treatment was progressively more effective from run 6 to run 8, as the temperature was lowered, even though the charcoal was becoming more used. When the temperature was elevated in run 9, the effectiveness of the treatment became nil and the foaming increased greatly. Run 10 demonstrated that the charcoal had been impaired; although the temperature of the run was the same as that of run 7, the foaming of the oil was intermediate between that of the samples of runs 7 and 9. Furthermore, run 11, made at the same temperature, was less effective than run 10. Hence the beneficial effect of low temperature and the gradual deterioration of the effectiveness of the charcoal are qualitatively demonstrated.

The effect of temperature is further confirmed by runs 4 and 5 (fig. 1(a)), in which the first, higher-temperature run is less effective than the later, lower-temperature run.

When run 6 (fig. 1(b)) is compared with run 5 (fig. 1(a)), both of which were made at 55° to 60° C, it appears that the treatment with once-used charcoal (run 5) is more effective than that with the new charcoal (run 6). When the very pronounced sequence of progressively lowered foaming in runs 6 and 7 (fig. 1(b)), where the temperature difference is slight, is considered, it seems probable that new charcoal is not so effective as that used once or twice.

The defoaming produced by the charcoal treatment is permanent and stable to the extent that, for $6\frac{1}{2}$ hours of air bubbling at 100°C , the volume increase of sample 4 from run 7 was the same, that is, 180 percent as compared with 650 percent for Aeroshell.

Following run 11, the charcoal was first washed with benzene, then pyridine. The pyridine elutriate so obtained was a powerful defoamer, exhibiting no foam at 100°C after 5 minutes of bubbling when present to the extent of only 1 percent in Aeroshell. When the concentration was reduced to 0.3 percent in Aeroshell, the volume increase at 100°C was 29 percent after 5 minutes of bubbling.

The elutriates removed from the charcoal by washing with benzene were recovered in only two instances, namely, following runs 4 and 5. These elutriates were foam inhibitors although not so powerful as the pyridine elutriate from the charcoal used in runs 6 to 11. The first benzene elutriate following run 4 showed an increase of foam volume of 594 percent after 30 minutes of air bubbling at 100°C (Aeroshell, 646 percent). The second elutriate following run 4, by the same test, increased the volume only 168 percent. The first and second benzene elutriates after run 5, by the same test, increased the volume 142 percent and 97 percent, respectively.

The data upon the foaming of the elutriates indicate that the foam-inhibiting substance closely adheres to the charcoal and that it accumulates as more oil is processed.

Treatment by Mixing Miscellaneous Sorbents with Oil

The results of the treatment of Aeroshell with selected sorbents are shown in table IV. Some of these sorbents had a definite effect in reducing the foam stability of Aeroshell, notably Celite. The same difficulty in prescribing an effective set of conditions for treatment may be expected to pertain to these sorbents as to charcoal. The fact that some defoaming effect may be obtained with them is significant.

A report was received that an oil company had defoamed oil during the process of filtering salt from the oil, and the effect was ascribed to sorption on the salt. A preparation of impalpable salt powder was prepared by precipitating salt from an alcoholic solution of sodium hydroxide with hydrochloric acid gas and drying the rinsed precipitate. This powder was mixed into Aeroshell 120 in a colloid mill in 0.2, 0.1, and 0.05 percent concentrations, and the foaming was tested before and after filtration. Salt did not affect the drainage rate of oil from the foam but slightly lowered the foam breaking rate. Under the conditions of the experiment, therefore, the sodium chloride powder slightly

stabilized the Aeroshell foam. It is believed that the defoaming effect ascribed to salt was due to another cause, possibly something analogous to the charcoal or Celite treatments previously described.

Treatment by Passing Oil through Miscellaneous Sorbents in Columns

The results of passing Aeroshell through columns packed with activated magnesium oxide, silica gel, and Porocel are graphically presented in figure 2 in the same manner as the charcoal results in figure 1. A charcoal curve is reproduced from figure 1(b) for comparison.

The roughly similar and peculiar shape of the three noncharcoal curves is striking. None of them approaches the effectiveness of the best charcoal results, but all have a range where the percentage increase in bubbling at 100° C for 8 minutes is reduced to one-half that of Aeroshell. The lowest foam volume, a single point on the magnesium oxide curve, is less than one-third that of Aeroshell.

Solvent Extraction of Lubricating Oils

The apparent removal of a foam-stabilizing component by a commercial phenol extraction process in lubricating-oil refinement has already been remarked (reference 1). The previously reported attempt to reduce foaming further by an additional phenol extraction was unsuccessful, but the defoaming result obtained in the commercial process was so marked that the process was repeated.

When tested by the method of aeration and evacuation, at room temperature, the phenol-extracted oils showed the following foam-stability results:

Oil	Foam stability
Standard Aviation 120	Slightly defoamed (D)
NACA Reference 120	Unchanged (E)
Aeroshell 120	Unchanged (E)

The repeatedly negative results may be taken to indicate that no further improvement upon the refined oil may be effected by additional phenol extractions.

Aeroshell 120 was subjected to extraction with two other solvents, liquid sulfur dioxide and aqueous 20 percent sodium hydroxide solution.

Neither of these extractions affected the foam stability of the oil that had been tested by the aeration and evacuation method at room temperature.

Effects of Heat on Foam Stability of Oils

From the beginning of the investigation, the marked effect of elevated temperature in rendering ineffective most agents which are foam inhibitors at room temperature has received much attention. As reported previously, chilling the oil to 0° C produced a temporary decrease in foaminess even when the oil temperature again reached that of the room (reference 1). In more recent experiments, a new effect of heat has been found. As subsequently described, heating the oil alone causes some change such that the foam-inhibiting action of a subsequently added elutriate from one of the charcoal treatments is sometimes impaired or even prevented.

One of the benzene elutriates from the treatment of Aeroshell 120 with charcoal at 0° C was found to be an effective foam inhibitor in the original Aeroshell when present in a concentration of only 1 percent. Heating this mixture to 100° C for 15 minutes permanently destroyed the foam-inhibiting action and restored the original foam stability of the Aeroshell. When the benzene elutriate was heated alone to 100° C and then added to Aeroshell in 1 percent concentration, it was as effective in decreasing foam stability as it was initially. Aeroshell 120 alone was heated for 1/2 hour at 100° C; then the benzene elutriate was

added. The foam stability of the mixture was tested at $\frac{1}{2}$ -hour intervals and found to be steadily increasing with age. At the end of 3 hours, the foam stability was about the same as that of the original Aeroshell. The final condition appeared to be permanent, and the oil retained its foam stability on further aging.

A reversible effect of a similar nature was found when a mixture of filtrate, petroleum-ether elutriate, benzene elutriate, and pyridine elutriate (1ALF plus 2ALEPE plus 7ALEPy), obtained from the first room-temperature treatment of oil with charcoal, was heated to 100° C and cooled to room temperature. The mixture had a reduced foam stability before heating. In the first room-temperature foam test after heating (by the aeration and evacuation method), the foam stability was the same as that of the original Aeroshell. However, upon subsequent tests the mixture recovered its defoamed property. This cycle of fluctuating foam stability exactly repeated itself when the sample was heated and cooled again.

These bits of evidence and the chilling effect previously reported indicate that the complex system of the oil reversibly changes character in a manner that affects foam stability at a temperature of 100° C but that certain materials, represented herein by the benzene elutriate, may be added which make the change permanent. The fact that the change is complex is indicated by the large time lag in the process.

Difference between First and Subsequent Foam-Stability Tests

In bubbling and aeration-evacuation foam tests, the first determination of foam stability after the oil has been poured in the apparatus shows a more stable foam than do subsequent tests. In all reports on foam stability, the results of the subsequent tests are cited. Various conjectures have been offered as to the cause of this effect. The following experiment is illuminating.

A sample of Aeroshell 120 was placed in the aeration and evacuation apparatus and tested for foam stability. As usual, the first foam was much more stable than subsequent ones. The oil was allowed to stand several hours, and the tests were repeated, with similar results. Following these tests, the system was evacuated, the stopcocks were carefully closed, and the system was allowed to stand 24 hours. The standard aeration and evacuation foaming test was then carried out, and the foam stability was found to be the same as the reproducible results obtained on subsequent tests. The experiment was repeated, except that the oil was heated to 100° C and was cooled under vacuum. As before, the excessive foam stability of the first test had been eliminated.

The excessive foam stability of the first foam test made on oil that had been exposed to the air for some time previous was thus shown definitely to be due to air dissolved in the oil. Furthermore, when oil is heated to 100° C and cooled in the presence of air, sufficient air is dissolved by the time the oil reaches the temperature of the room to give the oil the excessive foam stability of the first test. The diffusion of air through the highly viscous oil therefore appears surprisingly rapid.

DISCUSSION

Some of the reasons for the extreme difficulty in reproducing the results of treatments of small portions of oil with charcoal by heating in various vessels and filtering are shown by the curves for the column treatment. There are maximums and minimums in the foaming with time of treatment; as the temperature is raised, even below 100° C, the time curve is compressed and the optimum time of treatment becomes momentary, and the time during which any improvement will be observed is fairly short. With these facts previously unknown, the few excellent results obtained at first were very fortunate.

The complex shape of the curves (fig. 1) indicates that at least two processes are occurring at the charcoal surface. A first hypothesis was that a foam-stabilizing substance and a foam-inhibiting substance are present in each oil, with one or the other in greater concentration or held in some sort of complex that renders it inactive. The charcoal surface may then be effective either in sorbing the foamer or in releasing the defoamer from its complex, thus defoaming the oil.

This hypothesis has been useful in suggesting experiments that may be conducted but has failed to supply a completely consistent explanation for the observed phenomena.

A concentrated "foamer" has not been obtained from the oil, nor an oil of significantly increased foaming; the foam test methods are not well adapted to the measurement of increased foaming, but no oil has been obtained comparable with the modified oils in its ability to form a stable foam. Furthermore, within a fairly narrow range the unmodified lubricating oils are alike with regard to their foaming ability, for example, Aeroshell 120, Standard Aviation 120, and Gulf Airline 120. No lubricating oils have been found to foam much more than these unless they were modified. Such added foamers as are in modified oils have a strong preferential sorption, as shown experimentally by their segregation in the foam, while nothing seems to segregate in the foam of Aeroshell. There is no direct evidence as yet for the existence of a definite foam-enhancing substance in Aeroshell 120. From this information the conclusion that there is no separable foamer in Aeroshell is indicated, and the mechanism of the charcoal action should be so formulated as to avoid such a concept.

Sources of substances which may act as foam inhibitors need to be considered. Such sources are within the oil; the inhibitor may be produced by splitting of a weakly bonded compound, by an oxidation or a reduction at the charcoal surface, or by any combination of these. Since the production of an inhibitor is not a specific property of charcoal but is shown to a lesser extent by magnesium oxide, silica gel, Porocel, and possibly other sorbents, the chemical reduction of anything in the oil seems unlikely. The sensitivity of substances to oxidation is greatly increased by activated surfaces. However, it has been amply shown that the conditions for successful production of nonfoaming oil are highly specific. If the process is oxidative, therefore, it must be catalytic in nature and one that does not ordinarily occur (in an engine, for example). Splitting of some substance in the oil by the active surface to produce a foam inhibitor must also be a highly specific catalytic process.

In attempting to account for the shape of the curves in which foaming is plotted against time of treatment, it should be emphasized that the most powerful foam-inhibiting fractions are found closely associated with the charcoal and may be partly eluted with benzene and completely eluted with pyridine. The general shape of the curves may be qualitatively accounted for by supposing that some catalytic reaction produces a foam-inhibiting compound (or compounds) from substances in the oil, which are then preferentially sorbed on the active surface. The active surface would decrease in area as the foam inhibitor was produced and would become completely covered in time, blocking the formation of more inhibitor. Benzene elution partly restores the surface, possibly by removing substances more or less inert in the foaming effect,

which are less strongly sorbed than the inhibiting compounds. When the charcoal is no longer restored by benzene elution, its surface is covered by a strongly sorbed foam inhibitor.

Some of the curves show a double minimum, the first one fleeting. Another process, possibly the production of an unstable defoaming agent or one more strongly sorbed than that responsible for the later effect, is required to account for such a complexity. A definite and stepwise change in the active surface might also cause the double minimum.

From the general experimental method of oil treatment herein described, it is believed that a commercial process reasonably could be worked out empirically by those equipped to do so. Characterization of the foam-inhibiting substances has theoretical significance in the mechanism of oil foaming.

CONCLUDING REMARKS

The experimental work upon the defoaming of lubricating oil by recycling it through a charcoal column has progressed sufficiently that a method is known whereby a well-defoamed oil may be produced.

The column method of treating the oil with sorbents is a good method for studying the effect of changing conditions upon the action of the sorbents and for studying the mechanism of the reaction. Furthermore, a way is suggested by which the constituents of the oil may be separated, pertinent to a study of the effect of structure and composition upon foaming.

Several sorbents besides charcoal have been effective to a less extent in defoaming the oil. It is possible that under proper conditions, one or more of them might be more effective or more convenient to use than charcoal. They furnish an additional tool for separating, from the oil, components of interest to the foaming problem.

The fact that heating an aeronautical lubricating oil may alter the effectiveness of a subsequently added foam inhibitor proves the instability of some constituent of the system and indicates the necessity for caution and thoroughness in testing suggested remedies for foaming.

Stanford University

Stanford University, Calif., January 8, 1945

REFERENCE

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TABLE I.- CHARCOAL TREATMENT AT ROOM TEMPERATURE

Charcoal	Oil	Quantities (grams)	Remarks	Treated sample (1)	Foaming behavior
Storeroom	Aeroshell 120	20/100	Charcoal activated at low red in glass in vacuo	1A1F 2A1EPE 3A1EB 7A1EPy	D C-D ² and A-B ² A-B ³ C ⁴
Norit	Aeroshell 120	20/200	Charcoal activated just below red heat in iron in vacuo	4A2F 5A2EB 6A2EPE	C D ⁵ B ⁵
Norit	Aeroshell 120	15/200	Charcoal extracted with dioxane, petroleum ether; activated in glass in air 2 hr at 350° C	9A5F 10A5EPE	F B
Norit	Gulf Airline	15/200	Charcoal extracted with petroleum ether; activated 4 hr, 250° - 350° C, in glass in air	11G6F 12G6EPE	E E
Norit	Standard Aviation	15/200	Charcoal extracted with benzene; activated 4 hr, 350° - 400° C, in glass in air	12'S7F 13S7EPE 13'S7EB 20S7EPy	D A B ³ B ⁴

¹The following list is an explanation of sample numbers:

First integer serial number
 First letter initial of oil used (for example, A, Aeroshell 120,
 table II)
 Second integer charcoal number
 Final letter fraction description (F, filtrate; E, eluate;
 B, benzene; PE, petroleum ether; Py, pyridine)

²Filtrate plus petroleum ether eluate.

³Filtrate plus petroleum ether eluate plus benzene eluate.

⁴Filtrate plus petroleum ether eluate plus benzene eluate plus pyridine eluate.

⁵Filtrate plus benzene eluate.



TABLE I.- CHARCOAL TREATMENT AT ROOM TEMPERATURE - Continued

Charcoal	Oil	Quantities (grams)	Remarks	Treated sample	Foaming behavior
Norit	Aeroshell	15/108	Charcoal activated by heating in furnace 3 hr, 300° - 500° C	17A10F 18A10EPE 19A10EB 19'A10EPy	E B
Norit	Aeroshell	15/100	Charcoal activated by heating in furnace 3 hr, 300° - 500° C	21A10F 22A10EB 23A10EPy	E C
Norit	Aeroshell	5/100	Charcoal activated by heating in furnace 3 hr, 300° - 500° C	24A10F 25A10EB 26A10EPy	E B C
Norit	Aeroshell	1/102	Charcoal activated by heating in furnace 3 hr, 300° - 500° C	27A10F 28A10EB 29A10EPy	E- B
Norit	Aeroshell	1/124	Norit used with- out further treatment	30A11F 31A11EB 32A11EPy	D E ⁵
Nuchar C115	Aeroshell	1/128	Nuchar used with- out further treatment	30A11F 31A11EB 32A11EPy	E F ⁵
Nuchar CEE	Aeroshell	1/106	Nuchar used with- out further treatment	36A13F 37A13EB 38A13EPy	F F ⁵
Nuchar FAA	Aeroshell 120	1/108	Nuchar used with- out further treatment	39A14F 40A14EB 41A19EPy	E F ⁵
Norit	Aeroshell 120	1/114	Same charcoal as used for samples 17 to 29	42A10F 43A10EB 44A10EPy	E E

⁵Filtrate plus benzene eluate.

TABLE I.- CHARCOAL TREATMENT AT ROOM TEMPERATURE - Concluded

Charcoal	Oil	Quantities (grams)	Remarks	Treated sample	Foaming behavior
Norit	Aeroshell 120	5/113	Same charcoal as used for samples 17 to 29	45A10F 46A10EB 47A10EPy	E ⁶ E ⁶
Norit	Aeroshell 120	5/117	Norit used with- out further treatment	48A11F 49A11EB 50A11EPy	E ⁶ C ⁶
Norit	Aeroshell 120	5/101	Charcoal treat- ment carried out in presence of benzene, about 30 percent by volume	51A11FB 52A11EPy	D ⁶
Norit	Aeroshell 120	1/127	Charcoal activated in beaker in furnace, 30 min at 450° C	53A15F 54A15EB 55A15EPy	F ⁶ F ⁵ 6
Nuchar C115	Aeroshell 120	1/100	Charcoal activated in beaker in fur- nace, 30 min at 450° C	56A16F 57A16EB 58A16EPy	F ⁶ F ⁵ 6
Norit	Aeroshell 120	1/126	Charcoal activated in beaker in furnace, 4 hr at 450° C	59A19E 60A19EB 61A19EPy	E ⁶ C ⁵ 6
Nuchar C115	Aeroshell 120	1/133	Charcoal activated in beaker in furnace, 4 hr at 450° C	62A20F 63A20EB 64A20EPy	E ⁶ E ⁵ 6
Norit	Aeroshell 120	2/103	Charcoal activated in beaker in furnace, 4 hr, 150 - 700° C	65A21F 66A21EB	E ⁷ D ⁵ 7
Norit	Aeroshell 120	1/125	Charcoal activated in tin can in fur- nace 4 hr, 450° C	67A22F 68A22EB	E ⁷ E ⁵ 7

⁵ Fil. ate plus benzene eluate.⁶ Foam stability tested at room temperature by beating and evacuation method.⁷ Foam stability tested at 100° C by bubbling method.

TABLE II.- CHARCOAL TREATMENT AT ELEVATED TEMPERATURES

Charcoal	Oil	Quantities (grams)	Reaction vessel	Temperature (°C)	Time of heating (min)	Heating method	Tested sample	Foaming behavior ¹
Norit	Aeroshell	0.1/2	Test tube	High	3	Flame	69A11D	B
Do--	Aeroshell	.3/10	---do----	300	3	----do----	70A11D	
Do--	Aeroshell	.7/10	---do----	300	3	----do----	71A11D	B
Nuchar C115	Aeroshell	.3/10	---do----	300	3	----do----	72A12D	B
Do--	Standard Aviation	.3/10	---do----	300	3	----do----	73S12D	C
Do--	RPM Aviation	.3/10	---do----	300	3	----do----	74RPM12D	DD
Do--	Gulf Airline	.3/10	---do----	300	3	----do----	75G12D	E
Do--	Sinclair	.3/10	---do----	300	3	----do----	76Sin12D	D
Do--	Standard Synthetic	.3/10	---do----	300	3	----do----	77SS12D	C
Do--	Texaco	.3/10	---do----	300	3	----do----	78T12D	B
Do--	NACA Reference	.3/10	---do----	300	3	----do----	79N12D	B
Do--	Aeroshell 120	3/100	Flask	200	20	Oil bath	80A12D	E
Do--	-----do-----	3/100	---do----	200-300	40	----do----	81A12D	E
Do--	-----do-----	3/100	---do----	300	5	Flame	82A12D	E
Do--	-----do-----	3/100	---do----	300-395	40	Sand bath	83A12D	E
Do--	-----do-----	1/100	Continuous tube	Hot	Contact	Electrical winding	85A12F 86A12EB	E D
Norit	-----do-----	1/100	---do----	--do--	---do---	----do----	87A11F 88A11EB	E E ²
Nuchar C115	-----do-----	.5/52	100-cc beaker	310-350	30	Oven	89A12F 90A12EB	F C ²

¹Foam stability tested at 100° C by bubbling method.²Filtrate plus benzene eluate.

TABLE II.- CHARCOAL TREATMENT AT ELEVATED TEMPERATURES - Concluded

Charcoal	Oil	Quantities (grams)	Reaction vessel	Temperature (°C)	Time of heating (min)	Heating method	Tested sample	Foaming behavior ¹
Nuchar C115	Aeroshell 120	15/101	Continuous tube	Hot	Flash contact	Electrical winding	91A1212F 92A12EB	E ²
Do--	---do---	.3/46	100-cc beaker	375	30	Oven	93A12F 94A12EB	F C ²
Do--	---do---	.1/6.5	Test tube	Hot	2	Flame	95A12D	E ³
Do--	---do---	.25/10	Sealed, connected test tube	300	20	Oven	96A12F 97A12EB	F ⁴ D ⁵
Do--	---do---	0/10	20-cc beaker	300	20	----do----	98A12F 99A12EB	E ⁶ E ² 6
Do--	21A10F	0/10	----do---	300	20	----do----	100A12F 101A12EB	E ⁶ E ² 6
Do--	22A10EB	.3/10	----do---	300	10	----do----	104A12F 105A12EB	E ⁶ E ² 6
Do--	Aeroshell 120	1/12	Sealed evacuated test tube	310	15	----do----	102A12D	C ⁶
Do--	---do---	.5/10	----do---	305	15	----do----	103A12D	E ⁶

¹Foam stability tested at 100° C by bubbling method.²Filtrate plus benzene eluate.³Treated oil diluted with 4 volumes of Aeroshell.⁴Treated oil diluted with 1 volume of Aeroshell.⁵Treated oil diluted with 20 volumes of Aeroshell.⁶Foam stability tested at room temperature by aeration and evacuation method.

TABLE III.- CHARCOAL TREATMENT AT 0° C

[Foam stability was tested by aeration and evacuation method at room temperature]

Oil	Charcoal	Quantities		Initial filtrate	Foaming behavior of 1 percent BE ^a in Aeroshell	Foaming behavior of 1 percent BE ^a after heating and cooling
		Oil (ml)	Charcoal (grams)			
Aeroshell 120	Nuchar C-115	150	1.0	E	A	-
Aeroshell 120	Nuchar C-115	150	3.0	E	B	D
Aeroshell 120	Nuchar C-115	150	1.0	D	A-	D
Aeroshell 120	Darco G-60	150	1.0	E	A	D
Standard Aviation	Darco G-60	150	1.0	D	A	D
Aeroshell 120	^b Darco G-60	150	1.0	E	A	A
Aeroshell 120	Norit ^c (hot)		1.2	D	A	B
	Darco ^c (cold)	125	1.2	-	A-	B-

^aBenzene eluate.

^bThe oil was heated with charcoal to 33° C, then kept at 0° C for 4 hours, and filtered cold.

^cThe oil was treated first by the procedure at elevated temperature (345° C) with Norit, then treated by the procedure at low temperature (-30° C) with Darco, and filtered at 0° C.



TABLE IV.- TREATMENT WITH VARIOUS SORBENTS

[Foam stability tested at room temperature by aeration and evacuation method; sorbent (15 grams) was used to treat 100 grams of oil in contact 5 minutes at room temperature; filtered and adhering oil was eluted from sorbents with benzene, then pyridine]

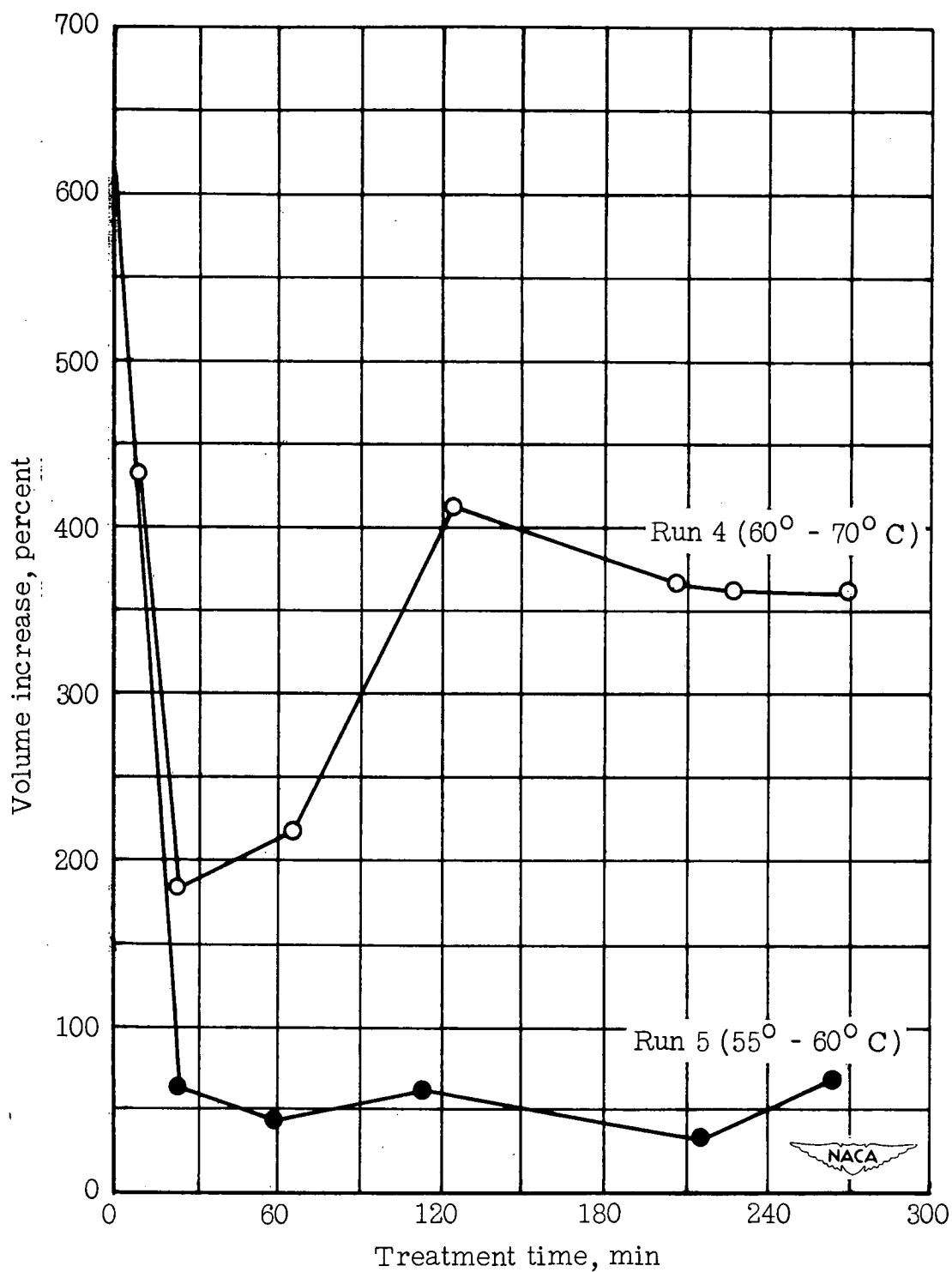
Sorbent	Oil fractions	Appearance	Foaming behavior
Cenco Infusorial Earth, benzene washed	Filtrate	Color, light; bloom, diminished	E
	Benzene eluate	Color, dark red; strong bloom	E ¹
	Pyridine eluate	Color, dark red; sweet odor	
Cenco Infusorial Earth, heated 2 hr at 400° C in furnace, benzene washed	Filtrate	Color slightly lighter than original	E
	Benzene eluate	Same as filtrate	E ¹
	Pyridine eluate	Color, dark red; viscous; sweet odor	
Cenco Infusorial Earth, washed with aqueous HCl, water rinse-dried 15 min at 400° C, benzene washed	Filtrate	Color slightly lighter than original	D
	Benzene eluate	Color, very dark red; opaque; strong bloom	D
	Pyridine eluate	Color, dark red; viscous; sweet odor	
Bentonite (Rosedale, Alberta), washed with aqueous HCl, oven-dried at 600° C (10 grams)	Filtrate	Same as original Aeroshell	D
	Benzene eluate	Color lighter than original	D ¹
Celite	Filtrate	Color slightly lighter than original	C-D
	Benzene eluate	Same as original	C-D ²
Activite	Filtrate	Color lighter than original	E
	Benzene eluate		E ¹
Kaolin (china clay)	Filtrate		D
	Benzene eluate		
	Pyridine eluate		
Celite, washed with boiling aqueous HCl, water-rinsed, dried at 100° C under vacuum	Filtrate ³	Same as original Aeroshell	D
	Benzene eluate		D ¹

¹Benzene eluate, 2 volumes; filtrate, 8 volumes.

²Benzene eluate, 1 volume; filtrate, 2 volumes.

³Primary filtration done with oil heated.





(a) Runs 4 and 5.

Figure 1.- Treatment of Aeroshell with charcoal in continuous circulating system. Foam stability tested at temperature of 100° C by bubbling method. Length of test, 30 minutes.

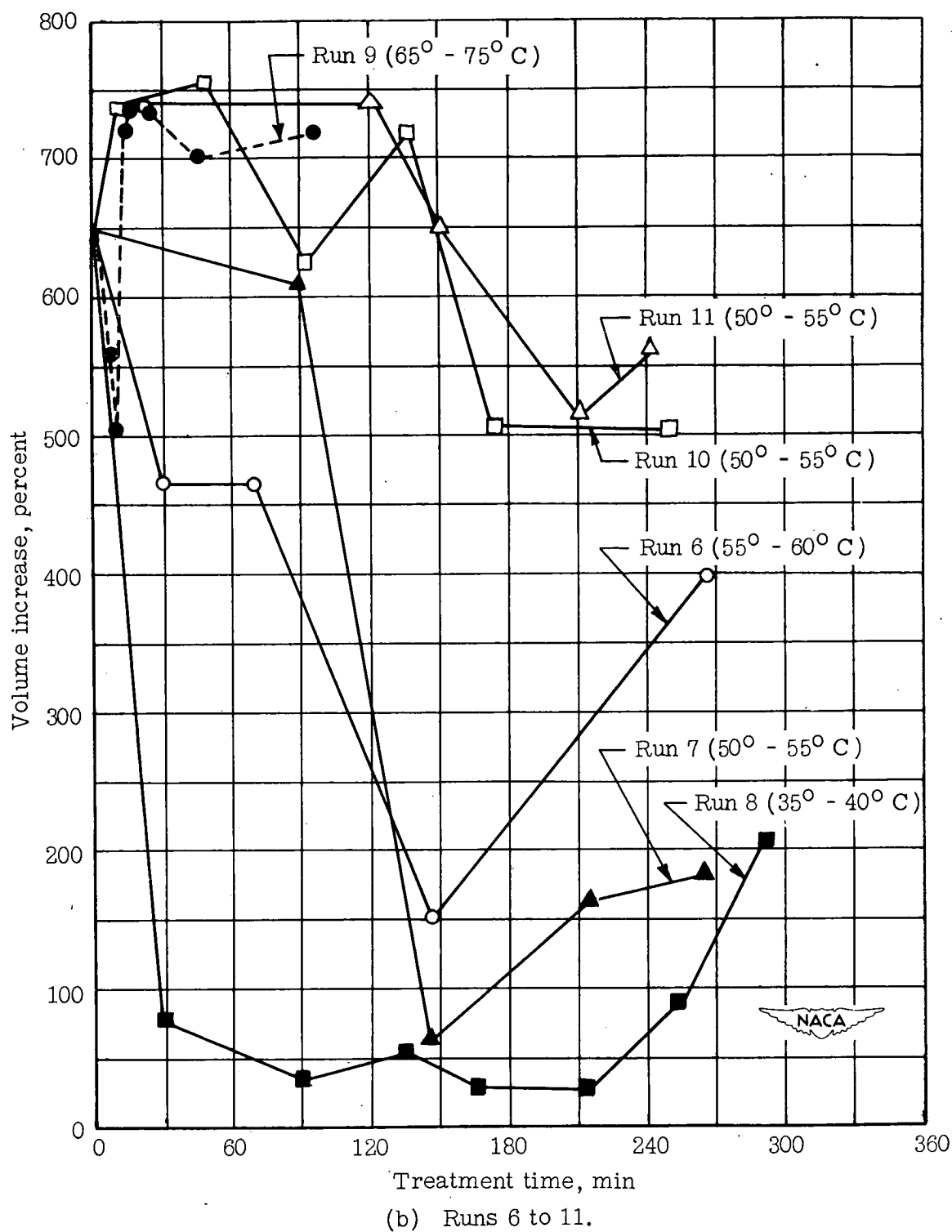


Figure 1.- Concluded.

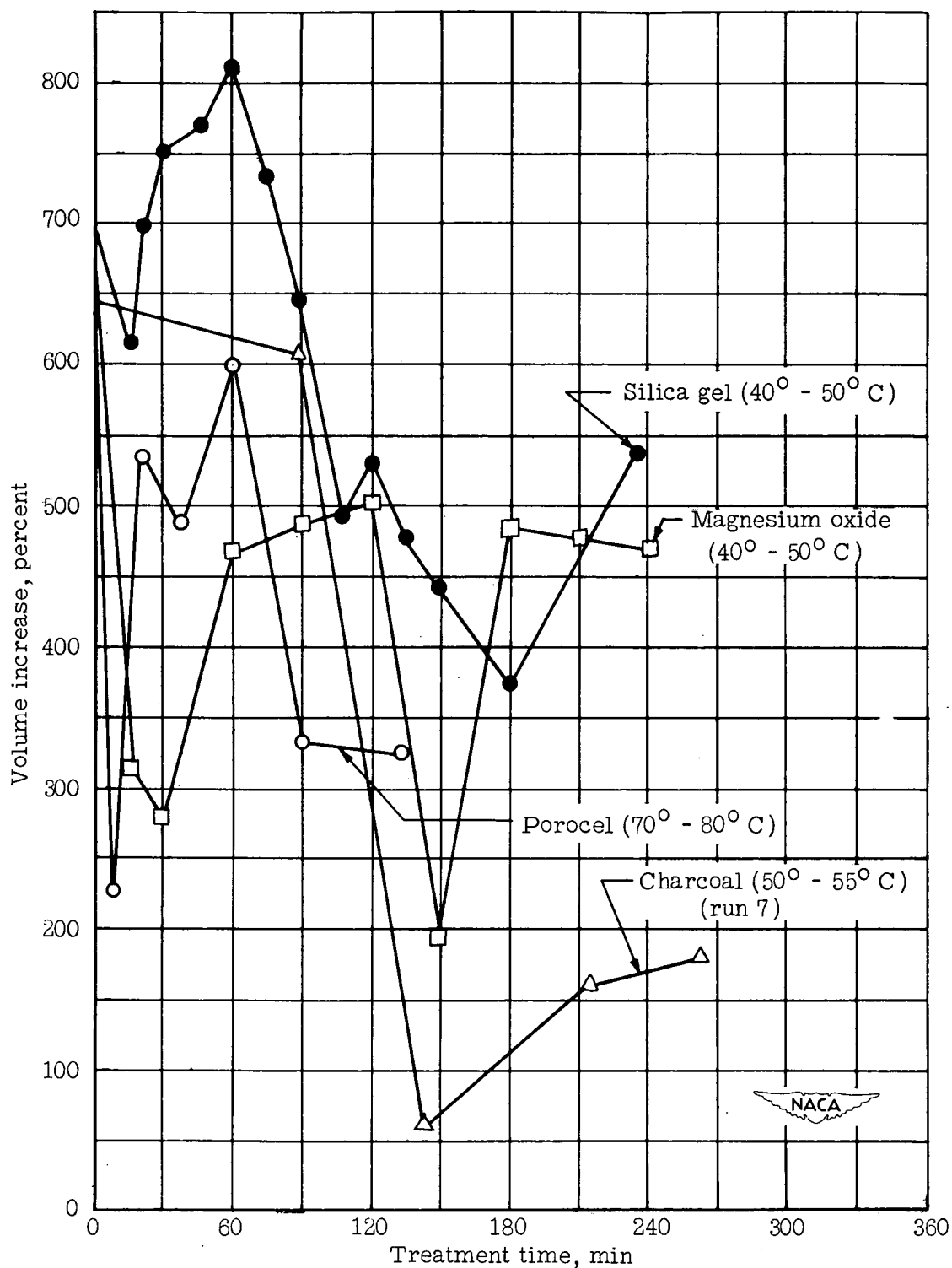


Figure 2.- Treatment of Aeroshell with varied adsorbents in continuous circulating system. Foam stability tested at temperature of 100° C by bubbling method. Length of test, 8 minutes.